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## Industrial production of coated glass: Future trends for expanding needs

Alain Arnaud \*

*Saint-Gobain Recherche, Boite Postale 135, 39 quai Lucien LeFranc, 93303 Aubervilliers Cedex, France*

### Abstract

Since decades, electroless plating has been used to produce mirrors. This extremely cheap process is now challenged by vacuum deposition and CVD (chemical vapor deposition) coating. In the fifties, architects began to design glass buildings and asked their suppliers for thermal protective products. Vacuum evaporation deposition, used for optics, was adapted for bigger surfaces. Then, boosted by increasing demand, two processes emerged for low cost production: direct pyrolysis on the float ribbon and magnetron sputtering. Today, heat regulating layers represent, by far, the biggest market in terms of sales and global potential. Production has reached many tens of million square meters per year. Sputtering and pyrolysis are still in competition. Both techniques made impressive progress. Sputtering lines reached capacities of many millions square meters per year handling automatically jumbo plates. During the same time, pyrolysis proposed multilayered structures and improved greatly deposition speed and uniformity. As the market continues to expand, new improvements are expected: for sputtering, higher speeds and the possibility of using non conductive targets, for pyrolysis, a decrease of the raw materials costs and an improvement in deposition yield. Other markets are emerging. They represent much smaller quantities but can take advantage of the improvement of the mass production technologies. In turn, as they need a high level of quality, they bring the opportunity of studying new deposition techniques and push the technology forward: transparent conductive coatings for displays, anti-solar coatings for automotive glazing, anti-reflective coatings, photovoltaics. Today, for these products low-pressure processes are used. When the market becomes larger, atmospheric CVD will be competitive. © 1997 Elsevier Science B.V.

### 1. Introduction

In terms of square meters of coated surface, the most important market of glass coating is not Low- $E$  ( $E$  = emissivity) or anti-solar glazing: it is containers.

Containers are coated by chemical vapor deposition processes (CVD) with a thin film of  $\text{SnO}_2$  or  $\text{TiO}_2$ . The purpose of this mineral coating combined

with a lubricating agent is to prevent scratches on the bottles.

Historically, the primary function of coating on glass has been decoration. Very early, enamelling techniques emerged and producers were confronted with the problems of thickness, visual aspect, mechanical resistance, adhesion and thermal treatment which are still today the problems of all those who produce coated glasses.

The first industrial process of coating on flat glass has been silvering by electroless plating. In this

\* Tel.: +33-1 48 39 58 00; fax: +33-1 48 34 74 16.

process silver is precipitated on the glass from an aqueous solution. [1]

The process works at ambient temperature. Deposition rate is high. The material losses are negligible. Glass panels with the full width of the float ribbon (Jumbo plates) can be treated at high speed. It is now possible to build high capacity lines in accordance with mass-market needs. These lines run close to their economic optimum.

## 2. Architectural coatings

### 2.1. Solar control

A new challenge arrived at the end of the sixties: the transparent heat regulating coating. For architectural and automotive use, glass is a material which has to stop everything: wind, rain, noise, burglars. Everything but light radiations in the range of 400 to 700 nm, which is the region of human eye sensitivity.

At that time, the float process reduced the production cost of thick glass [2], boosting the glass facades market. Glass, even colored, is rather transparent for near infrared, and solar load of the new buildings

was too high and/or light transmission was too low (Fig. 1).

Glass manufacturers proposed improved tinted glasses, with more selectivity. Color in transmission was present and, as energy was absorbed in the glass, the solar factor was not excellent. Then transparent coatings were proposed to improve the situation. Different coating techniques were known in optics and microelectronics:

- vacuum evaporation, [3-7]
- pyrolysis. [8,9]

The market of coated glass increased rapidly. Improvements occurred in both techniques.

Vacuum evaporation which had problems of homogeneity and durability of the coatings was replaced by vacuum sputtering, as a major innovation [10-12]. It was possible to coat big pieces of glass with metals and oxides.

Liquid pyrolysis, first used to coat tempered glass during tempering process, was adapted to continuous treatment of glass ribbon at the exit or inside the float line.

### 2.2. Thermal insulation

The development of the anti-solar market was followed by that of thermal insulation. In a standard

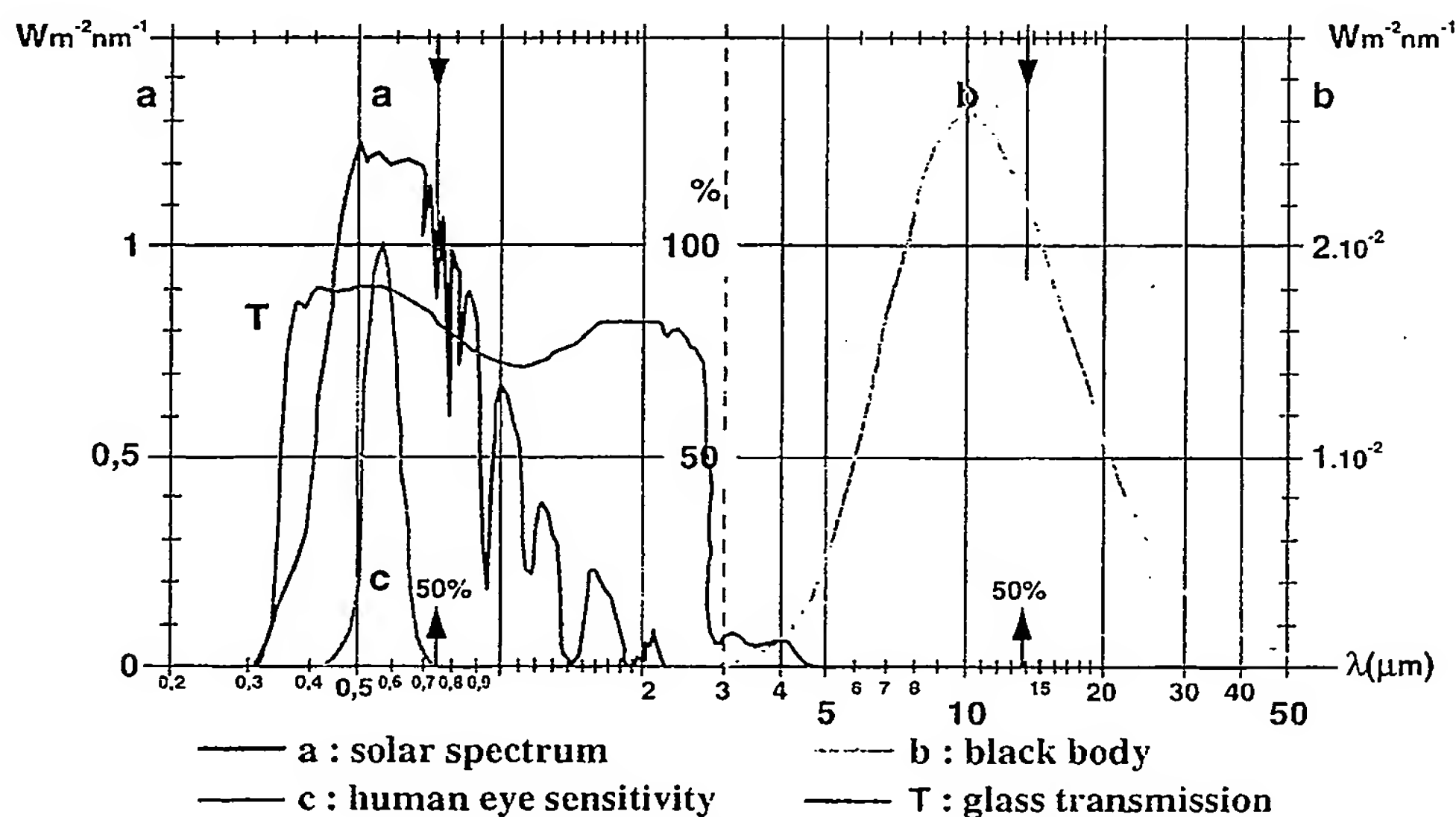


Fig. 1. Solar and ambient radiation.

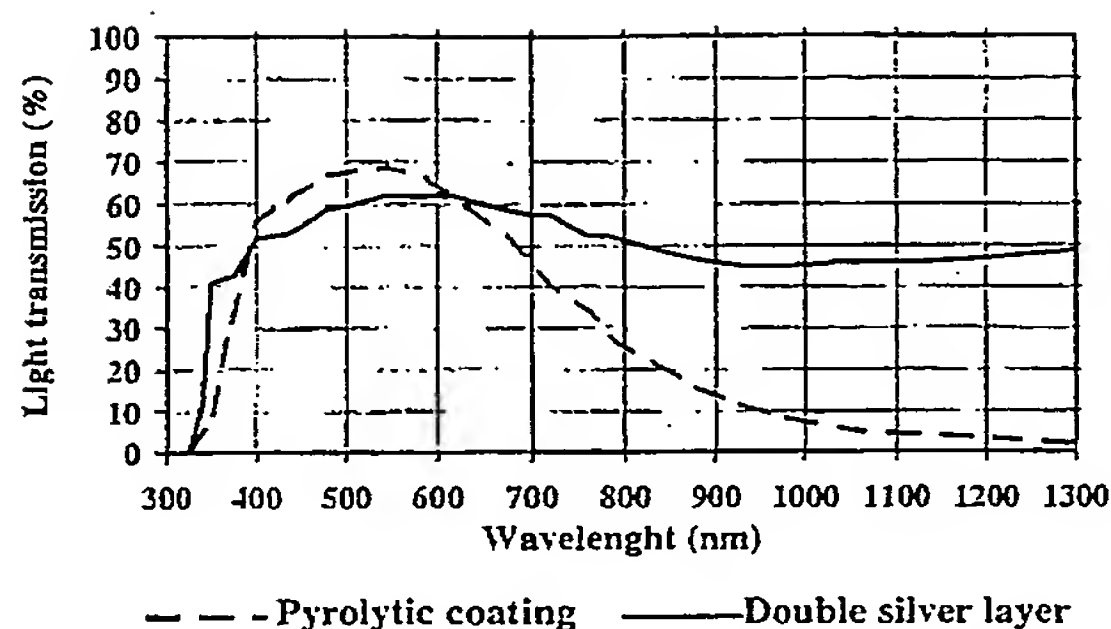


Fig. 2. Light transmission of an antisolar double glazing.

double glazing, about 40% of energy is lost through thermal radiation in the wavelength range of  $10\ \mu\text{m}$  (Fig. 2). The development of photovoltaic cells and liquid crystal display had needed transparent conductive electrodes of fluorine doped tin oxide ( $\text{SnO}_2:\text{F}$ ) [13] and indium tin oxide (ITO) [14,15]. Due to their electrical conductivity, these coatings were good heat reflectors [16].

Silver containing anti-solar coatings were also heat reflectors. With a thinner silver layer and two oxide anti-reflexives coatings, it was possible to obtain a very effective heat reflector with good light transmission [17].

At the end of the seventies, the cost decrease due to the market expansion made it possible to propose competitive products on the insulation market.

Compared to that of anti-solar glazing, the thermal insulation market has a much higher potential. In Europe today, the anti-solar market represents about 5 millions  $\text{m}^2$ . Heat reflectors represent more than 30 millions  $\text{m}^2$ .

But market penetration is still small. In Northern Europe heat regulating coatings become standard for new residential buildings. It is developing also for renovation. In Southern Europe, sales are limited. Renovation has a 'tremendous potential': there are in Europe 2 billion  $\text{m}^2$  of windows and only a few percent are equipped with heat reflecting glazing. For the home owner, changing the glazing is very expensive, but fitting techniques are improving and various systems are proposed.

The economic and ecological impact is important: with all European windows equipped with heat reflecting double glazing, energy saving would be one

billion gigajoules and  $\text{CO}_2$  emissions in the atmosphere would be reduced by 100 millions of tons [18].

Which performances are needed for a heat reflective glazing:

(1) High transmission for natural light. This effect is the primary function of the window.

(2) Reflection for the  $10\ \mu\text{m}$  range (infrared light). This reflection governs insulating performance.

(3) Neutral color in transmission and reflection

(4) Mechanical and chemical durability. When assembled in double glazing, the coating is protected against attack. But handling, transport and manufacturing are adapted to standard glass and are very demanding for coatings. And as the coating is on the inner face of the double glazing, the frame will be glued on it.

(5) Temperability. In Continental Europe, most of double glazing are annealed glass. The market for tempered products is small. In English speaking countries, a big part of double glazing is made of tempered glass.

(6) Heat transmission in the near infrared. This transmission provides free solar heating in winter season, but with risk of overheating in summer.

### 2.3. Production

To meet that demand, two processes are in use: pyrolysis and vacuum coating. They could follow the market development and remain competitive.

#### 2.3.1. Pyrolysis

Pyrolysis is installed on float lines of 15 millions  $\text{m}^2$  per year capacity. Even if open time is not 100%, potential capacity is large compared to the European market size of 30 millions  $\text{m}^2$  per year.

Ribbon speed is imposed. Fixed costs of the float line are so high that any speed reduction would induce prohibitive cost increase.

The most popular glass thickness in Europe is 4 mm which give a ribbon speed around 12 m/min. Fortunately, due to high temperatures of the tin bath, the deposition speed is very high. Compared to deposition rates of a few tens of nanometers at one meter per minute, deposition rates for pyrolysis are many thousands of nanometers for the same speed.

The pyrolytic coating is a semi-conductor. Its electrical conductivity is not very high. Heat reflection averages 85%. Higher reflection can be obtained but light transmission would decrease and cost would increase.

Color neutrality is obtained by a color suppressing layer whose thickness has to be carefully controlled.

Chemical and mechanical durability are clearly the strong points of pyrolytic coatings. The coating is even harder than glass itself. It is temperable.

Pyrolytic coatings are relatively transparent to near infrared which provides good solar gain to the window.

#### 2.3.2. Vacuum sputtering

Current annual capacity of vacuum sputtering lines exceed 5 million m<sup>2</sup> which is less than float production but largely in line with market needs.

The coating consists of a thin silver film sandwiched between two transparent oxide layers whose function is to improve light transmission [17]. Thermal reflection can be very high, up to 95% which is actually close to the theoretical limit. Light transmission is also excellent. To obtain reflection neutrality, the thickness of the three layers has to be carefully controlled.

Mechanical durability, quite satisfactory for final use, is rather critical for transformer needs. When exposed to ambient air, specifically in southern countries where the moisture content of the factory atmospheres are greater, the coatings begin to corrode after few weeks. In the same way handling has to be done carefully to avoid scratches. Where plants use currently these products, these problems are under control with a limited extra cost.

For tempering, a special product is needed to avoid changing color or performance during the high temperature process. In the near infrared, the transmission is rather poor so, solar gain is limited. This transmission can be adjusted, and coatings with higher silver thickness can be heat insulators in winter and anti-solar systems in summer.

#### 2.3.3. Double layer coatings

It is necessary to mention a product, very interesting for office buildings but applicable also to any air conditioned room. This product is made of two silver coatings with three transparent layers. This added

complexity has its cost but the product is a very good reflector for thermal radiations and solar infrared. It has also a very good light transmission, and is well adapted to continental climate where the temperature change is important between winter and summer. It is well known in the United States. It needs specific production lines but production cost is rapidly decreasing with capacity increase.

#### 2.3.4. Ways for improvement

For pyrolytic coatings, the deposition rate is higher than for sputtered ones. It should be still higher to decrease the size of the float equipment. The crystallographic structure of the coating should be improved to obtain a better heat reflection and a better light transmission. More efforts are needed on chemicals used to produce the coating. Material yield is rather low. The major part of active molecules remain in the effluent which has to be treated and recycled. Some deposits build up on the equipment which need expensive cleaning.

For sputtering, the investment cost increases with production capacity and represent a large part of the total cost. Deposition rate has to be increased and evacuation time has to be decreased. Material yield of the cathode is not sufficient and rotating cathodes have been slow to reach industrial performance. Cleaning the line and changing the cathodes require a long time and restart the production need quality adjustment. Then, for both processes, the color control must be improved by measurement of the layers thickness and a better width control of the process.

### 3. Automotive coatings

Conductive transparent coatings are used on aircraft transparencies to heat the glass and prevent frost formation. Generally evaporated or sputtered ITO (indium tin oxide) is used [19]. Attempts have been made to propose heated laminated glass for car and industrial production has been experienced. The power and the voltage required were difficult to obtain from a standard electric supply for cars.

Silver coatings were proposed for heated windshields but also for anti-solar neutral laminated glazing [19]. Very efficient, these products are popular for Japanese backlites and special American wind-



shields. As long as they were made by sputtering on bent glass, production cost remained high. Big efforts have been made to produce coatings on flat glass able to sustain the aggression of the bending process, requiring deep knowledge of chemistry and mechanics of thin films.

#### 4. Electronics

Two sectors of electronic industry require transparent electrodes on glass:

- photovoltaic cells,
- liquid crystal displays.

The first one exhibits a continuous growth but due to high production and storage cost of photovoltaic electricity, there has been no substitution to conventional production facilities. Today, the world market represents less than 1 million m<sup>2</sup> per year. Producers use a transparent coating very close to the one used for low-E glass. High conductivity, high light transmission, and defect free surface are required. This coating can be produced by on line CVD on glass ribbon or by plasma enhanced chemical vapor deposition processes (PECVD) on individual substrates.

The liquid crystal display market is rapidly growing with a wide range of quality requirements. Sputtered ITO is used for all applications. In the low end

segment, horizontal sputtering machines can produce large surfaces at low cost. But, for the flat panel displays industry, the optical quality has to be excellent. Debris falling from planar cathodes create pin holes on the substrates. For this segment, ITO is coated at high temperature on small size substrates with vertical machines. To prevent migration of sodium from glass to liquid crystal, a silica layer is required between glass and ITO coating. The sputtering of this silica layer has been a big challenge to sputtering industry: silicon cathode is difficult to realize and as silica is a good insulator, it disturbs the electron flow in the coating chamber. Different devices are now proposed to obtain reasonable deposition rates of insulator layers.

#### 5. Anti-reflective

Anti-reflective coatings are widely used in optics. They consist of a stack of low and high refractive index layers [20]. For small surfaces, evaporation is the most suitable process but, as sputtering was performing better for insulator deposition, and especially SiO<sub>2</sub> and TiO<sub>2</sub>, bigger surfaces were to be considered. In fact, the first market for big size anti-reflective coating was pioneered by the sol-gel process to make high grade storefronts or display

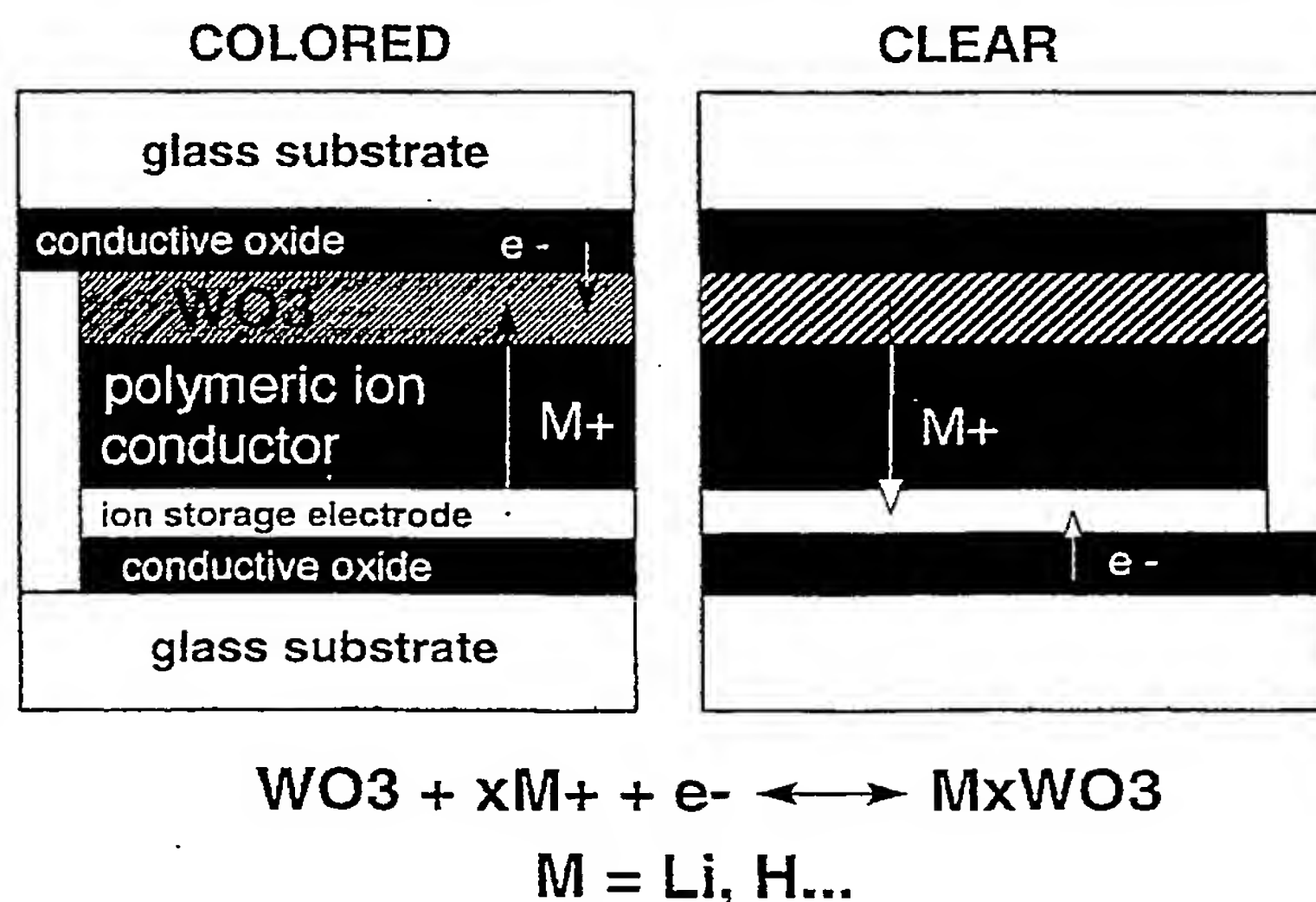


Fig. 3. Structure of an electrochromic window.

boxes [21]. Due to the high cost of the product, the market remained limited.

High grade CRT tubes are now proposed with an anti-reflective coating, made by sputtering, and anti-reflective flat glass is about to be proposed. Due to low deposition rates and high thickness accuracy requirements, the new coating will remain rather expensive but cost decrease will improve its market potential.

## 6. Electrochromics

Windows of the future, intelligent windows are the terms used to describe variable transmission glazing [22].

Two products are currently in use:

- Privalite panels based on liquid crystal emulsion,
- Electrochromic rear view mirrors.

Systems based on organic materials use ITO electrodes of standard quality.

Systems based on ion coloration of  $\text{WO}_3$  use very sophisticated stacks of oxide materials (Fig. 3) [23].

In this application, the coating is not a passive material. It forms a chemical reactor where ion migration induces coloration and discoloration. In that case, the structure of the material is of great importance.

Magnetron sputtering is well adapted for this emerging market:

- quantities produced will be limited at the beginning,
- many materials can be deposited by this technique,
- material structure can be adapted thanks to various parameters adjustments.

Other deposition techniques are explored, such as sol-gel which is also flexible in terms of chemical composition and structure. In that case, the relatively weak structure of sol-gel coating would not be a major problem since, these products are laminated and encapsulated.

## 7. Conclusion

Among the various coating techniques: electroless plating, evaporation, sol-gel, plasma enhanced

chemical vapor deposition (PECVD), atmospheric CVD, and sputtering, two of them have emerged to reach mass production of widespread products: magnetron sputtering and on-line pyrolysis.

Both are able to treat large size plates, to reach a high level of control, to produce multiple layers products, to accommodate different materials.

For very high quality products, sputtering is superior since on line pyrolysis works in the standard float line environment which is not (not yet?) that of a clean room. On line pyrolysis is appreciated for mass production of many millions square meters per year but sputtering is very efficient too on that segment. The future of these technologies will depend on the efforts devoted to their development.

New markets are emerging, they will benefit of the improvements made on the process control, the speed of deposition and the cost of equipment.

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